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Study of optical and photocatalytic properties of titanium oxide films with different oxidation degree

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The results of studies of the optical and photocatalytic properties of titanium oxide films deposited by vacuum-arc evaporation in an oxygen-containing atmosphere are presented. It was experimentally shown that films of different degrees of oxidation are formed during deposition, depending on the amount of oxygen flow entering the working chamber. The results of studies of the obtained films showed that the films obtained in a transitional mode between the deposition of metallic Ti films and dielectric TiO_2 films have the maximum photocatalytic activity. This deposition mode is observed at the oxygen flow into the working chamber from 9 to 12 cm^3/min

Keywords: titanium dioxide, anatase, photocatalytic activity.

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Titanium oxide thin films have a number of unique properties: chemical resistance, a sufficiently high refractive index in the visible range, the have photo-catalytic and anticorrosive properties This combination of properties have drawn a great application prospect for their use in optical devices, integrated photonics, gas-sensitive sensors as well as their use in air and water purification devices from harmful organic compounds [1–5]. The purpose of this article is to study the effect of the technological regime of titanium oxide thin films deposition by the means of cathodic arc deposition on their optical and photocatalytic properties.

Thin films of titanium oxide were obtained at the experimental installation ?PVR-1? (national research Tomsk polytechnic university, Russia). [6]. Set of devices used for deposition: ion source, Sablev?s type cathode arc evaporator, planetary substrates holder, substrates heating system and bias voltage system.

TTitanium oxide thin films were deposited on glass and silicon substrates with an area of 12cm2 and 2.25 cm^2 cm respectively, as well as on polished stainless steel substrates with an area of 6.25 cm^2 in size. The distance between arc evaporator and substrates was 35 cm. Before deposition substrates were cleaned by the means of boiling in peroxide-ammonia solution followed by washing in isopropyl alcohol and distilled water. Finish cleaning was made by the beam of Ar ions from the ion source in the operating chamber before deposition (voltage: 2.5 kV; current: 40 mA; time of cleaning: 10 min).

Thin films were deposited by DC cathode arc evaporator with various oxygen flow rates (from 6 to 15 cm^3/min). The argon flow rate was constant (3.6 cm^3/min). The resulting pressure in the operating chamber was about 0.2 Pa. The arc discharge current was 90 A. The time of deposition was 10 minutes for glass and silicon substrates and 60 minutes for steel substrates.

Refractive index, absorption index and thickness of the obtained titanium oxide fims were measured by the Spectral ellipsometry complex „Ellips-1891 SAG“ (Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sci-ences). Results are shown in the table 1.

Studies have shown that the increase of the oxygen flow rate $Q(O_2)$ leads to the increase of the refractive index. Known published literature shows that titanium oxide thin films have a sufficiently high refractive index, which is different for different forms: n = 2.288 for anatase, n = 2.583 for brookite, n = 2.609 for rutile [7]. It can be concluded that coatings obtained with oxygen flow rate $Q(O_2) = 15\,cm^3$/min are completely amorphous and have an excess of metallic titanium in their structure. Films obtained at oxygen flow rates of 6 and 7.5 cm^3/min have an excess of titanium metal atoms in their structure, are amorphous and have low photo-catalytic activity.

The phase composition of the titanium oxide thin films was studied by Shimadzu XRD-7000S diffractometer (Shimadzu, Japan). X-ray diffraction analysis of the samples Nos. 1 and 2 shows the absence of titanium oxide phase in them. These films consist of a fine-grained phase, which forms the amorphous structure. The rutile phase (up to 82%) prevails in thin films deposited with the oxygen flow rate in the range from 9–15 cm^3/min. The size of the coherent scattering region is 4 nm. Obtained results are in good agreement with published data [8,9], which said that the mixture of anatase and rutile phases or mostly the anatase phase is observed at oxygen flow rate of 20 cm^3/min.

Refraction and absorption indices and thicknesses of titanium oxide films

Sample number	Oxygen flow rate $Q(O_2)$, cm^3/min	Refraction index n	Absorption index k	Film thickness, nm	Deposition rate, μm/h
1	6	1.4	1.5	314.4	1.886
2	7.5	1.63	1.2	301.3	1.808
3	9	2.15	0.47	254.5	1.527
4	10.5	2.22	0.33	244.6	1.468
5	12	2.3	0.23	241.2	1.447
6	13.5	2.37	0.17	143.5	0.861
7	15	2.45	0.12	131.4	0.788

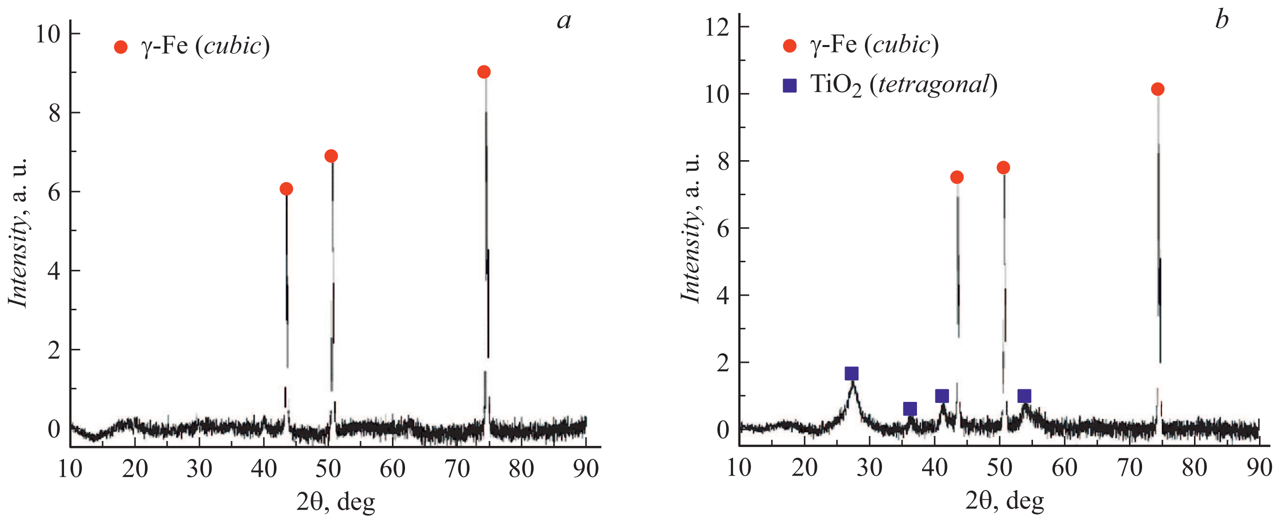

Figure 1. XRD spectra of the thin film samples: *a* — Sample No. 1, oxygen flow rate $Q(O_2) = 6\,cm^3$/min; *b* — sample No. 7, oxygen flow rate $Q(O_2) = 15\,cm^3$/min.

The results of the X-ray diffraction analysis for samples Nos. 1 and 7 are shown in Fig. 1.

The morphology of the surface of the thin films was studied by a contactless profilometer MicroMeasure 3DStation (STIL, France). Thin films obtained at an oxygen flow rate in the range from 9–12 cm^3/min have the largest roughness. Such result can be explained by increasing of the internal mechanical stresses in the films due to their thickness. Mixture of the rutile phase and amorphous phase in the structure of the thin films also increases internal mechanical stresses. The growth of mechanical stresses leads to the formation of microcracks and the formation of pores in the film.

The microrelief is smoothened and the structural and morphological uniformity of titanium oxide thin films increases with an increase of oxygen flow rate up to 15 cm^3/min. Maximal RMS roughness of the samples (R_a) does not exceed 0.046 μm, maximal roughness (R_z) does not exceed 0.36 mm. These results allow us to assume that there are no large microdroplets on the coating that affect the results of measuring of the photocatalytic activity.

The obtained titanium oxide films on glass substrates were examined for photocatalytic ac-tivity according to the method described in [9–11]. Studies of the photocatalytic activity of titanium oxide films were carried out after 30, 60, and 90 min UV irradiation. The results of the study were obtained at a wavelength of 588 nm and are shown in the Fig. 2.

Three regions can be recognized on the dependence of the photocatalytic activity of the thin films on the oxygen flow rate during their deposition. There is a smooth transition mode from the titanium metal films deposition mode to the tita-nium oxide thin films deposition mode with the increase in oxygen flow rate.

Films obtained at oxygen flow rates of 6 and 7.5 cm^3/min have an excess of titanium metal atoms in their structure, are amorphous and have low photo-catalytic activity. Films deposited at oxygen flow rate of more than 13 cm^3/min also show low photocatalytic activity due to their small thickness despite the fact that the tita-nium oxide phase in the coatings is up to 82%.

The transitional titanium oxide films obtained with an oxygen flow rate in the range from 9-12 cm^3/min have the

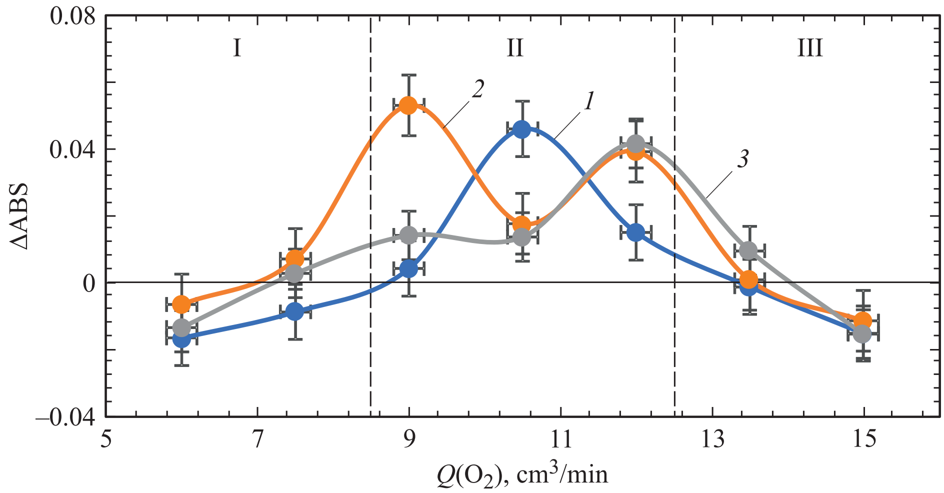

Figure 2. Dependence of the photocatalytic activity of titanium oxide films on the oxygen flow rate dur-ing their deposition after UV irradiation: 30 (*1*), 60 (*2*), and 90 min (*3*).

maximum photocatalytic activity. There are several reasons for that. Firstly, these films are thicker, which means they have higher photocatalytic activity. Secondly, titanium oxide thin films obtained in this mode have a more rough and porous struc-ture, which increases their active surface area. Thirdly, crystal rutile phase appears in these thin films, which significantly increases the pho-tocatalytic properties of coatings relative to amorphous films obtained with low oxygen flows.

Thus, the photocatalytic activity of titanium oxide thin films obtained by the cathode arc deposition strongly depends on the modes of their production, particularly on the oxygen flow rate, thickness, as well as surface roughness and porosity. Thin films obtained in transitional mode have maximal photocatalytic activity. In this mode the cathode surface remains free of oxide but the amount of oxygen is sufficient enough to form a crystal phase. The optimal mode for formation of the photocatalytic titanium oxide thin films by the means of cathode arc evaporation in this study was provided with oxygen flow rate in the range from 9–12 cm^3/min.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal rela-tionships that could have appeared to influence the work reported in this paper.

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